

**Pennsylvania Water Resources Research Center,  
Penn State Institutes of Energy and the  
Environment  
Annual Technical Report  
FY 2010**

# Introduction

Authorized by Congress as one of the nation's 54 water resources research institutes, the Pennsylvania Water Resources Research Center (PA-WRRC) emphasizes the role of research, education, and outreach in advancing water issues. The PA-WRRC supports research and information transfer projects at academic institutions across Pennsylvania, aimed at addressing water resources problems of importance in the state and region.

*Research Projects.* Four projects supported during FY10 were research -oriented, addressing unanswered questions in water resources. These cover topics such as quantifying the effects of atmospheric deposition on water quality (PI Boyer), predicting mercury accumulation in watersheds across the state (PI Drohan), advancing in water treatment through membrane filtration (PI Dempsey), and understanding emerging contaminants that escape water treatment (PI Achary).

*Information Transfer Projects.* Two projects supported during FY10 were information-transfer oriented, making research based information available to stakeholders statewide. One of these provided public education opportunities associated with the Marcellus Shale exploration (PI Swistock), while the other brought researchers together from across the state to a water symposium (PI Boyer), aiming to network and to consider the role of research in advancing water resources issues.

*Education.* Numerous students (8) and postdocs (1) were supported or partially supported Within the PA-WRRC projects this fiscal year; listed below in the format: (Principal Investigator of the USGS 104B project), Student name, Department, Academic Institution. *Masters:* 1) Robbie Welford (Dempsey), Department of Civil & Environmental Engineering, Penn State University; 2) Xia Shang (Dempsey), Department of Civil & Environmental Engineering, Penn State University; 3) Emilie Erich (Drohan), Department of Crop & Soil Sciences, Penn State University; 4) Lidiia Iiavorivska (Boyer), School of Forest Resources, Penn State University; 5) Michelle Cleveland (Swistock), Ecology Program, Penn State University; 6) Benjamin Conway, Temple University School of Medicine. *Doctoral:* 1) Shawn Rummel (Swistock), Ecology Program, Penn State University; 2) Candice Johnson (Achary), Temple University School of Medicine. *Postdoc:* 1) Hyunchul Kim (Dempsey), Department of Civil & Environmental Engineering, Penn State University.

# Research Program Introduction

None.

# USGS Award No. G09AP00118 Long-term Responses of Stream Chemistry to Changes in Atmospheric Deposition in Mid-Appalachian Forests of Pennsylvania

## Basic Information

<b>Title:</b>	USGS Award No. G09AP00118 Long-term Responses of Stream Chemistry to Changes in Atmospheric Deposition in Mid-Appalachian Forests of Pennsylvania
<b>Project Number:</b>	2009PA120S
<b>Start Date:</b>	7/1/2009
<b>End Date:</b>	6/30/2014
<b>Funding Source:</b>	Supplemental
<b>Congressional District:</b>	5
<b>Research Category:</b>	Climate and Hydrologic Processes
<b>Focus Category:</b>	None, None, None
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Elizabeth Boyer, David Russell DeWalle

## Publications

1. Boyer, E.W., J.W. Grimm, K.S. Horner, J.S. Lynch, and M.A. Borden (2010). Atmospheric Deposition in Pennsylvania: Spatial and Temporal Variations 2009. Report prepared for the Pennsylvania Department of Environmental Protection by the Pennsylvania Water Resources Research Center, 255 p.
2. Boyer, E.W., J.W. Grimm, K.S. Horner, and M.A. Borden (2010). Atmospheric Mercury Deposition in Pennsylvania in 2009. Report prepared for the Pennsylvania Department of Environmental Protection by the Pennsylvania Water Resources Research Center, 65 p.

## **PROJECT TITLE & PRINCIPAL INVESTIGATORS**

Long-term Responses of Stream Chemistry to Changes in Atmospheric Deposition in Mid-Appalachian Forests of Pennsylvania

Elizabeth W. Boyer and David R. DeWalle, School Forest Resources, Pennsylvania State University

## **PROBLEM & RESEARCH OBJECTIVES**

This research project seeks to quantify and understand the unique long-term response of stream chemistry to reductions in atmospheric deposition that have been observed over the past three decades on five forested catchments in the Mid-Appalachian mountain region of Pennsylvania (PA). These catchments are part of the US Environmental Protection Agency's (USEPA) Long-Term Monitoring of Ecosystems (LTM) program. This network of forested, headwater catchments serves to determine status and trends in stream water quality in the eastern USA region, in response to chronic acidification via atmospheric deposition and to other vectors of change such as climatic variability.

Here, five acid-sensitive catchments in the Appalachian mountains of Pennsylvania are studied to quantify trends in surface water physical and chemical properties, in response to the effects produced by changing emissions of atmospheric pollutants on the biogeochemical cycles within the stream catchments. For forested streams of this region, the primary effects of atmospheric pollutants will be associated with acidic deposition and climate change. Responses of mid-Appalachian streams to acidic deposition involve chronic or episodic changes in the acid-base status of surface waters. Surface water acidification occurs when concentrations of strong-acid anions (sulfate and nitrate) increase relative to concentrations of base cations (calcium, magnesium, potassium, and sodium ions) in a stream. The result of this shift in acid-base status will be a depression in stream pH, possibly to a range associated with adverse effects on fish and other aquatic life. Responses of mid-Appalachian streams to climate change may be manifest in a number of ways. Increasing temperatures and shifting rainfall patterns will affect all aspects of the water cycle in these catchments. Changes in water flux through catchment soils can produce trends in surface water chemistry. Changes in episodic (storm) flow can alter chemical equilibria in streams. Changes in stream temperature can have enormous significance for freshwater organisms, and can affect temperature dependent chemical reactions.

## METHODOLOGY

The five study catchments are located on the Northern Appalachian Plateau in the state of Pennsylvania. These catchments can be characterized as relatively undisturbed, mixed-hardwood forest basins. The basins are second-order streams that were not glaciated during the last major period of glaciation, and range from 5-11 km<sup>2</sup> in area, and from 701 to 893 m in maximum elevation. Benner Run and Linn Run catchments are part of state forest land administered by the Pennsylvania Department of Conservation and Natural Resources, Bureau of Forestry. Baldwin Creek, Stone Run and Roberts Run basins are located on lands managed by the Pennsylvania Game Commission. Arrangements have been made with these agencies to access these lands on a regular basis to conduct this study.

We conducted stream sampling, stream gaging, and laboratory for monthly samples from these five forested streams, which are acid-sensitive and are poorly buffered. On each stream water sample, we measured the following items:

Table 1: Summary of analytical laboratory water quality techniques.

Parameter	Methodology	Equipment
Temperature	Resistance thermometry	YSI Telethermometer
pH	EPA Electrometric (150.1)*	Beckman 360
ANC-Gran titration	EPA Titrimetric*	Radiometer automated titration unit
Specific Conductance	EPA Specific Conductance (120.1)*	YSI Conductance Meter Model 32
Sulfate, nitrate and chloride	EPA Ion Chromatography (300.0)*	Dionex Ion Chromatography Unit ICS 3000
Ammonium	Automated Phenate Method**	SEAL AQ2 Discrete Analyzer
Dissolved Metals		Perkin Elmer Atomic Absorption Spectrophotometer, Model 5100
Calcium	EPA AA Direct Aspiration (215.1)*	“
Magnesium	EPA AA Direct Aspiration (242.1)*	“
Potassium	EPA AA Direct Aspiration (258.1)*	“
Sodium	EPA AA Direct Aspiration (273.1)*	“
Aluminum – total dissolved	EPA AA Furnace (202.2)*	“
Silica	Molybdate –Reactive Silica**	SEAL AQ2 Discrete Analyzer
DOC	EPA 415.2 (low level)*	OI Analytical TOC Analyzer 1010
DIC	EPA 415.2 (low level)*	OI Analytical TOC Analyzer 1010

\* Method referenced to US EPA (1983)

\*\* Method referenced to Clesceri et al. (1998)

## **PRINCIPAL FINDINGS AND SIGNIFICANCE**

As forested ecosystems of the eastern USA continue to adjust to dynamic changes in atmospheric deposition, long term monitoring is critical in order to understand effects on water quality. We continued measuring basic stream chemistry and stream flow in five forested streams of Pennsylvania, to further establish a record of change.

Acid deposition can have serious effects on aquatic ecosystems. For example, acidified waters can impair the ability of fish gills to extract oxygen from water and change the mobility of certain trace metals (e.g., aluminum, cadmium, manganese, iron, arsenic, mercury), which in turn can place fish and other species sensitive to these metals at risk (NAPAP, 1991). The susceptibility of a water body to acidification depends on the ability of the water and catchment soils to neutralize the acid deposition it receives. The best measure of this ability is acid neutralizing capacity (ANC), which characterizes the amount of dissolved compounds that will counteract acidity. Every body of water has a measurable ANC, which depends largely on the surrounding catchment's physical characteristics, such as geology, soils, and size. The ANC of a body of water reflects the relative proportions of positive and negative ions entering the water from sources such as atmospheric inputs and the soil and bedrock surrounding and underlying the water body. The higher the ANC, the more acid a water body can neutralize and the less susceptible it is to acidification. Considering long term results over the past three decades in the five study catchments, gradual decreases in stream sulfate and increases in ANC levels in streams have been noted, largely in response to the reductions in emissions associated with the Clean Air Act Amendments of 1990.

Similarly, nitrogen (N) retention efficiency, the percentage of N inputs from the atmosphere and other sources that are stored in catchment soils or lost to the atmosphere via denitrification, is an important characteristic of forest catchment ecosystems that controls delivery of N to receiving waters. Nitrogen budget studies in forested ecosystems reveal that retention efficiencies on relatively-undisturbed forested catchments commonly exceed 70% and may reach  $\geq 90\%$ . In these Pennsylvania catchments, N retention efficiency generally increased over the last few decades (1989-2006) associated with declining atmospheric deposition during this period.

The project supported one graduate student during this period (Lida Iiavorivska, Masters of Forest Resources, School of Forest Resources, Penn State University).

# Simultaneous Removal of Phosphorous and Organic Acids using Magnetic Ion Exchange Resin (MIEX) Treatment and Alum Prior to Micron Filtration

## Basic Information

<b>Title:</b>	Simultaneous Removal of Phosphorous and Organic Acids using Magnetic Ion Exchange Resin (MIEX) Treatment and Alum Prior to Micron Filtration
<b>Project Number:</b>	2010PA124B
<b>Start Date:</b>	3/1/2010
<b>End Date:</b>	2/28/2011
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	PA-005
<b>Research Category:</b>	Engineering
<b>Focus Category:</b>	Wastewater, None, None
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Brian Andrew Dempsey, Brian Andrew Dempsey

## Publication

1. Kim, Hyun-Chul; Brian A. Dempsey, 2010, Removal of organic acids from EfOM using anion exchange resins and consequent reduction of fouling in UF and MF, J. Membrane Science 364(2010), 325-330.



## **PROJECT TITLE & PRINCIPAL INVESTIGATORS**

Simultaneous removal of phosphorous and organic acids using magnetic ion exchange resin (MIEX) treatment and alum prior to micron filtration

Brian A. Dempsey and Hyun-chul Kim, Department of Civil and Environmental Engineering, Pennsylvania State University

## **PROBLEM & RESEARCH OBJECTIVES**

The main goal was to achieve simultaneous removal of total phosphorus (TP) and membrane fouling natural organic matter (NOM) during wastewater treatment using magnetic ion exchange resin (MIEX).

MIEX is an alternative to biological nutrient removal (BNR) for decreasing TP. MIEX contains a quaternary amine cationic polymer adhered to Fe-oxide precipitates that are magnetic allowing rapid separation and recovery. BNR cannot consistently attain the TP goal of <0.3 mg/L without coagulants. Use of coagulants results in excess sludge production, high costs, and additional wastewater effluent discharge of sulfate and aluminum. Membrane treatment is also increasing in use since it provides positive removal of particles including pathogens and particulate P. We have shown that MIEX is effective in removing the NOM constituents that cause membrane fouling.

Thus the research objectives were the following: (1) determine the effects of competing anions and NOM on the removal of TP from wastewater effluent organic matter (EfOM); (2) identify the removals of TP using several treatment modes; and (3) find the best methods for administering MIEX in a treatment facility, especially considering column operation or addition during rapid-mix with subsequent sedimentation (or not) prior to passage of the wastewater through low-pressure membrane filters.

## **METHODOLOGY**

Experiments were all performed at bench-scale using column and jar-testing operations followed by membrane filtration. In Phase 1 the independent variables were MIEX concentration, EfOM concentration, anion concentrations (nitrate and sulfate), NOM concentration, TP, pH. In Phase 2 both complete-mix and fixed-bed column were investigated with results monitored by water quality, resistance to filtration, and flux recovery with cleaning. In Phase 3 the MIEX and membrane treatment processes were optimized for removal of TP and reduction in membrane fouling.

## **PRINCIPAL FINDINGS AND SIGNIFICANCE**

Batch tests for removal of TP and fouling using MIEX, IRA-958, or coagulants. This phase of the project was designed to identify the feasibility for applying MIEX and other strategies for simultaneous removal of TP and membrane foulants from wastewater effluent.

1. MIEX removal of membrane foulants was not affected by the anions bicarbonate, phosphate, nitrate, and sulfate.

2. MIEX removal of TP in batch tests was adversely affected by higher concentrations of sulfate and alkalinity.
3. MIEX removal of TP was not affected by lower molecular-weight (MW) EfOM organic acids but was adversely affected by high MW alginates that are a constituent of some wastewaters.
4. IRA-958 removal of TP was not affected by sulfate or alkalinity.
5. Aluminum chlorohydrate (ACH) coagulant removal of TP was adversely affected by alginates but not by low MW EfOM organic acids.
6. IRA-958 removal of alginates was increased in the presence of higher alkalinity, while MIEX removal of alginates was not affected by alkalinity.
7. In the absence of high sulfate, alkalinity, or alginate, MIEX was more effective than IRA-958 for removal of both TP and membrane foulants despite smaller charge capacity of MIEX.
8. The batch experiments demonstrated that MIEX or other anion exchange resins could effectively remove both TP and membrane foulants for some conditions.

Column studies. This phase of the work was designed to evaluate the effectiveness of cationic exchange resins under the best possible conditions, passage through a bed of resin as opposed to the cheaper alternative of directly adding resin into a flowing stream.

1. Passage of wastewater effluent through a fixed-bed column of MIEX resulted in nearly complete elimination of short-term fouling of PVDF MF and PES UF membranes, even for permeate flux exceeding  $300 \text{ Lm}^{-2}\text{hr}^{-1}$  which is up to an order of magnitude higher flux than typically used. Thus the cost of installing and operating a bed of resin could be partially offset by the increased loading and decreased capital and operating costs for operating membrane filters.
2. The reduced fouling coincided with nearly complete removal of particles, colloids, and HPO/HPI organic acids. MIEX in fixed-bed form also removed >50% of HPO base/neutrals, less than a third of TPI base/neutrals, and no HPI base/neutrals. This means that the quality of filtered water (with respect to organic content) would be significantly superior if a bed of MIEX resin were used ahead of the membranes.
3. The removal of TP from wastewater effluent from University Area Joint Authority (UAJA) was much greater than predicted from batch tests of synthetic waters (reported above) or from batch tests of UAJA water. This is particularly significant because UAJA uses alum as a coagulant thus adding high sulfate concentration to the wastewater.
4. The resin capacity for TP and membrane foulants was simultaneously exhausted. This would result in more efficient and cost-effective operation of a column of resin.
5. MIEX was more effective than other resins for simultaneous removal of TP and membrane foulants.

Rapid-mix addition of MIEX. MIEX can be added directly to the wastewater stream resulting in decreased capital costs and perhaps in decreased operating costs. Treatment options that were considered included direct addition of MIEX without intermediate removal by sedimentation resulting in accumulation on the membrane surface, addition of MIEX followed by

sedimentation so that most of the MIEX did not accumulate on the membrane surface, and addition of MIEX with simultaneous addition

1. Complete-mix additions of MIEX, alum, or MIEX/alum reduced TP and membrane fouling but to a lesser extent than for fixed-bed MIEX.
2. There was also poorer removal of particles, colloids, and HPO/HPI acids compared to fixed-bed MIEX.
3. The best combination for simultaneous removal of TP and EfOM after complete mix used 15 mL/L of MIEX and only 1 mg/L of Al.
4. Complete-mix additions of MIEX with simultaneous low coagulant doses and membrane filtration resulted in permeate TP < 0.3 mg/L.
5. These results indicate that fixed-bed or fluidized-bed operation of MIEX ahead of MF or UF should be considered for full-scale treatment.

The results demonstrate that MIEX or other anion-exchange resin can be used in combination with other TP removal strategies, resulting in lower discharge concentrations and greater reliability for compliance with TP goals. The simultaneous decrease in fouling of low-pressure membranes could result in increased permeate fluxes and decreased cost for construction and operation of membrane systems.

## **STUDENTS & POSTDOCS SUPPORTED**

### Masters students

Robbie Wolford (expected graduation as M.S. in Env. Eng., August 2011)

Xia Shang (expected graduation as M.S. in Env. Eng., December 2011)

### Post-Doc

Hyunchul Kim

# Predicting Total Mercury in Pennsylvania Soils in Order to Predict Pennsylvania Watersheds with the Highest Total Mercury Contents

## Basic Information

<b>Title:</b>	Predicting Total Mercury in Pennsylvania Soils in Order to Predict Pennsylvania Watersheds with the Highest Total Mercury Contents
<b>Project Number:</b>	2010PA125B
<b>Start Date:</b>	3/1/2010
<b>End Date:</b>	2/28/2011
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	PA-005
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Water Quality, Sediments, None
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Pat Drohan

## Publications

1. Erich, E., P.J. Drohan, R.L. Ellis, M.E. Collins, M. Payne, D. Surabian. 2010. Subaqueous soils: their identification and importance in ecosystem management. Soil Use and Management 26:245-252.
2. Erich, Emilie, 2010, Pedogenic fate and transport of total mercury across subaerial and subaqueous soils in an Appalachian Plateau impoundment, M.S., Crop and Soil Sciences Dept., Penn State University, University Park, PA, 260 pp.

## PROJECT TITLE & PRINCIPAL INVESTIGATOR

Predicting total mercury in Pennsylvania soils in order to predict potential stream Hg loading.  
Patrick Drohan and others, Department of Crop and Soil Sciences, Pennsylvania State University

## PROBLEM & RESEARCH OBJECTIVES

Regional, mercury (Hg) emitting, coal-fired power plants, manufacturing and waste incineration, along with high amounts of annual precipitation, result in Pennsylvania receiving some of the heaviest loads of atmospheric Hg deposition in the United States. While much research has examined Hg accumulation in water bodies, there has been limited assessment of Hg accumulation in soils, especially over a great aerial extent and with depth. This proposal addresses the identified gap in knowledge by examining atmospheric deposition loads and soil Hg contents across Pennsylvania, in order to identify watersheds at greatest risk to Hg pollution.

## METHODOLOGY

### Objective 1: Derive soil Hg loading across Pennsylvania Benchmark soils

The USDA-NRCS Soil Survey program has identified specific soil series in the United States as Benchmark soils. A benchmark soil is: one of large extent within one or more major land resource areas (MLRA); has a large amount of soil physical, chemical, and mineralogical data; has special importance to one or more significant land uses; or is of significant ecological importance (USDA-NRCS, 2009). In completing Objective 1, we will use archived Benchmark soil series pedons and associated archived characterization data from the Penn State Soil Characterization Database, to develop soil loadings, base line critical concentration estimates for Hg in Pennsylvania Benchmark soil series, and to identify watersheds potentially prone to heavy Hg-loading.

Because the archived pedons represent a point in time approximately 30 years ago, our calculation will represent base line data and thus be extremely useful to future users of soil survey data in comparing Hg accumulation in soils over time. Hg-T analysis of full pedons will also provide us with an estimate of parent material Hg contributions; parent material Hg contributions are very poorly understood in the Northeast U.S.

*Methods.* Twenty one Benchmark series occur in Pennsylvania. In the Penn State Soil Characterization Database (PSUSCD [Ciolkosz and Thurman, 1992]), nineteen of these series have archived pedons (139 total pedons [Figure 1], 1086 horizons: Berks (13 pedons); Brinkerton (4); Buchanan (8); Cavode (9); Clarksburg (10); Clymer (5); Duffield (9); Ernest (8); Gilpin (4); Hazleton (17); Lackawanna (10); Leck Kill (10); Morris (5); Penn (5); Readington (5); Weikert (2); Westmoreland (4); and Wharton (3).

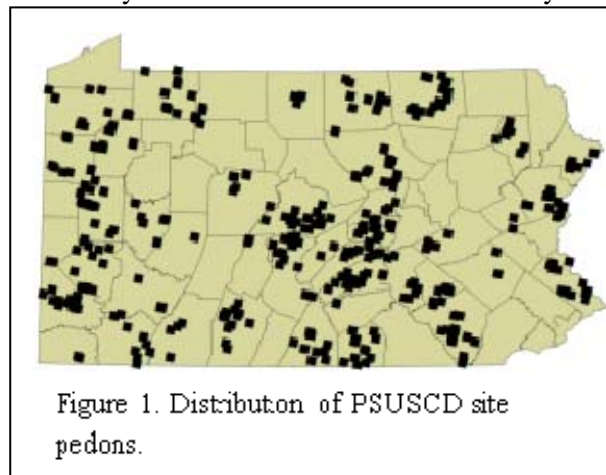


Figure 1. Distribution of PSUSCD site pedons.

These series represent dominant Pennsylvania parent materials:

1. limestone (10 pedons);
2. argillaceous limestone (9);
3. gray and brown acid sandstone (30);
4. gray and brown acid shale (40);
5. calcareous shale (4);
6. acid till (13) and
7. red acid shale (33).

Eight of the series have fragipans and the series distribution spans drainage classes from poorly drained to well drained. Eight pedons were sampled after 1973 but before 1983; remaining pedons were all sampled prior to 1973.

Hg-T will be measured via a Milestone DMA-80 Direct Mercury Analyzer (EPA method 7473 protocol [US EPA 2000]). Analysis will be completed by the Penn State Institutes of Energy and the Environment (PSIEE) water quality laboratory, University Park, PA under direction of collaborator Dr. Elizabeth Boyer. Archived profile data (horizon thickness and bulk density (available for each horizon)) will be used to derive soil Hg contents, and existing soil horizon physical, chemical and mineralogical data will be used in conjunction to develop Benchmark series representative regression relationships to predict Hg-T content in soils throughout state. Using results from previous soil-related Hg research as a guide for variable analysis (Aastrup et al., 1991; Lindqvist et al., 1991; Hultberg et al., 1995; Schwesig et al., 1991), we will specifically examine Hg-T vs.: soil profile morphology (sub-horizon type, redoximorphic feature presence; depth and thickness); bulk density; particle size trends (sub-fractions too); Total N; cation exchange capacity; base saturation; pH; organic carbon content; Al, Fe, Mn; and XRD derived mineralogy (all parameters for every horizon are already measured and thus available for statistical analyses).

Calculations from de Vries et al. (2007) will be used to calculate Hg-T critical loadings for soil horizons. C-horizon Hg-T data will be statistically compared across parent materials using a non-parametric Kruskal Wallace multiple comparisons analysis (Minitab, 2005) to assess natural Hg-T in soils. In addition, similar comparisons will be made for surface horizons to infer atmospheric deposition loadings representative for the time of sampling.

*Expected Outcome.* Objective 1 allows us to take advantage of the 30+ years of archived Soil Survey pedon data and extend soil survey interpretations for Pennsylvania to include Hg-T. These calculations will assist us in evaluating statewide Hg loading developed in Objective 2 and provide an extremely valuable future data set for Hg monitoring in the Northeast. This methodology will allow us to evaluate hypotheses one and three while also helping pose new hypotheses. Results from Objective 1 will be used to present one refereed journal article on Hg-T trends across Pennsylvania Benchmark series, parent materials, and drainage classes and provide valuable data for future research proposals.

*Objective 2. 2. Develop models of Hg loading for Pennsylvania soils and identify watersheds with potentially high Hg loadings.*

Benchmark soil series Hg-T contents developed in Objective 1 will be used to develop three soil Hg content models for PA Benchmark soils.

First, a *surface horizon's model* will be developed using surface O and A horizon data and second a *parent material model* will be developed using C horizon data. These two models will provide a base line approximation of soil Hg-T across Pennsylvania. These two soil models will then be coupled with existing Hg deposition data provided by collaborator Dr. Elizabeth Boyer, to construct a *Hg critical loading model* across the state for all soils using the digital Statewide Soil Geographic Database (SSURGO).

*Methods. Mercury deposition data:* Hg deposition data will be provided by the Pennsylvania Atmospheric Deposition Research Program, led by Dr. Elizabeth Boyer. Boyer and colleagues have monitored wet atmospheric Hg deposition weekly in Pennsylvania since 2000 to quantify spatial and temporal patterns of Hg and to understand consequences of Hg emissions in the atmosphere (Boyer et al. 2009). Boyer operates 9 sites at present in PA (with 2 additional planned for 2010), all of which are contributed to the National Atmospheric Deposition Program's Mercury Deposition Network (MDN). Both measured data (from the point monitoring locations) and modeled data (see below) will be developed for use in our state-wide model of accumulation of Hg in soils (Figure 2). Where needed for spatial analysis, the ArcGIS platform will be used.

*Model development and data delivery:* We will first develop a map of contemporary wet atmospheric Hg deposition at high resolution across Pennsylvania (quarterly and annually), using a modification of methods put forth by Grimm and Lynch (2004) and Golden and Boyer (2008). A statistical model is developed that combines detailed spatial and topographic data with precipitation observations from a dense network of rain gage stations to produce high-resolution estimates of precipitation across PA. This in turn is combined with the monitoring data of Hg in precipitation from the Pennsylvania MDN sites, producing estimates of wet deposition that have been shown to be more accurate than those obtained using traditional two-dimensional interpolation algorithms (Grimm and Lynch 2004).

Dry Hg deposition is not operationally measured at the MDN sites (in PA or nationwide), and thus we will estimate the dry component of Hg deposition throughout PA on the basis of the wet deposition, imposing ratios of dry/wet deposition that are simulated from a simulation model.

We will quantify ratios of dry/wet deposition across PA using contemporary Hg simulations from NOAA/EPA's Community Multiscale Air Quality model, under current base scenarios (Bullock & Brehme 2002). Our resulting high-resolution maps of total (wet + dry) Hg deposition in Pennsylvania will be used as a proxy for Hg loadings to soils across Pennsylvania. Using data from Objective 1 and 2, Critical Concentrations for all soils in the state will be estimated on the basis of the pedogenic characteristics.

Last, in collaboration with Dr. Anthony Buda of the USDA-ARS and Dr. Elizabeth Boyer, model results of soil Hg loading, in conjunction with State Soil Geographic (SSURGO) digital soil data, will be used to develop Hg loadings for all soils in Pennsylvania. Using identified relationships between soils and Hg-T developed in Objective 1, we will model Hg-T for other soils in the SSURGO database not analyzed in our research. We will then use our soil loadings in conjunction with a dataset of Pennsylvania watersheds [9,895 watersheds] (PADER/USGS, 1989; Seaber, 1987) to identify watersheds at the greatest risk of Hg-T loading (natural and anthropogenic). Natural loadings will be considered derived from soils in our model where parent material contributions are high.

#### *Expected Outcome.*

We will construct a statewide assessment of potential Hg loading to soils and watersheds in Pennsylvania. We believe this will be the first model to attempt such an analysis over a geographic area the size of Pennsylvania. This methodology will allow us to further evaluate hypotheses one and three and evaluate hypothesis two. In addition, this research will help us pose new hypotheses.

The accessibility of the model to others will insure ease of availability and maximize usefulness for future research. Results from this objective will be combined into two refereed journal articles: one on Hg-T soil critical loading across Pennsylvania and one on watershed loading. Results from this objective will also provide valuable data for future research proposals.

Our models of probable Hg accumulation, and the associated soils at risk to Hg critical loading will be *first approximations* -- limited by the available data, and are affected by vast heterogeneity in Hg in the air (sources, emissions, transport, deposition) and on the landscape (terrain, soils, wetness, etc). We will urge appropriate caution with regard to the utility and interpretation of the results. However, this will be the first attempt at statewide projections of Hg risk, and our results will be useful at generating interest

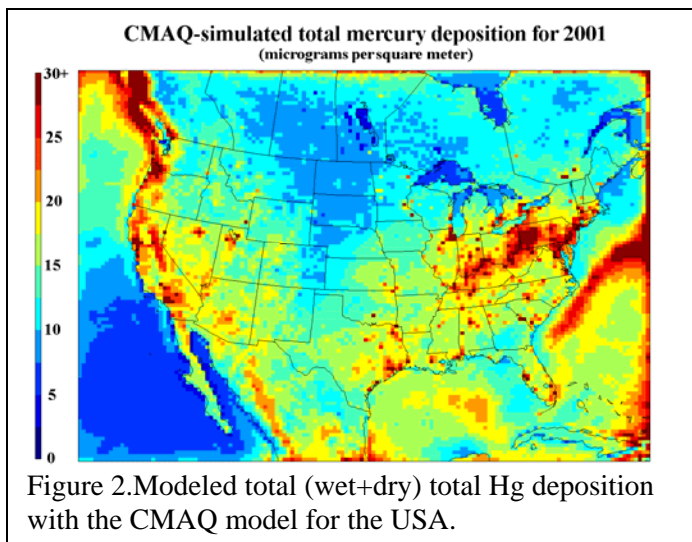


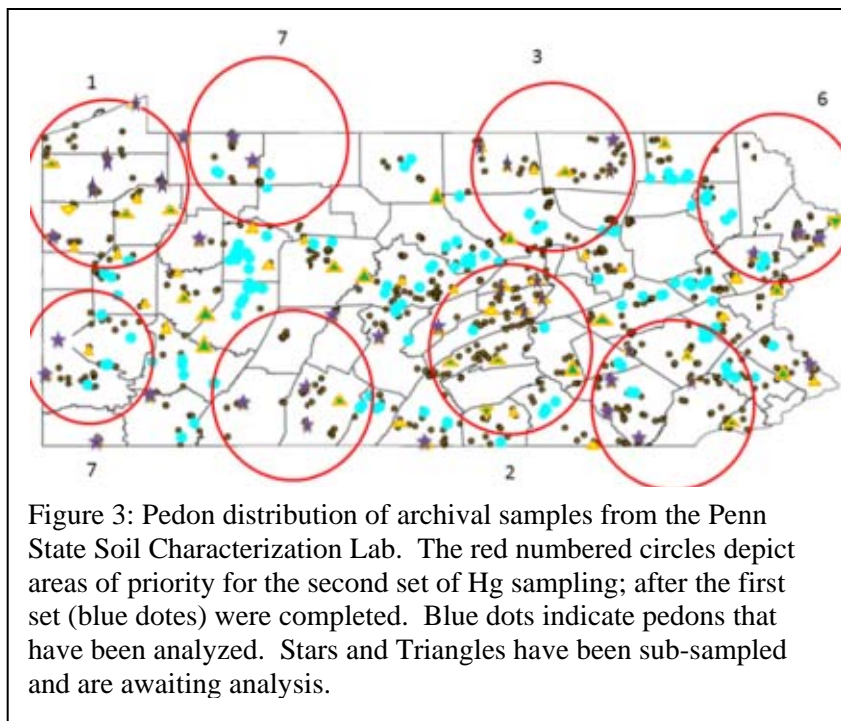
Figure 2. Modeled total (wet+dry) total Hg deposition with the CMAQ model for the USA.



in the problem and will generate *testable* hypotheses about the accumulation of Hg in soils of Pennsylvania that can be followed in subsequent studies.

## PRINCIPAL FINDINGS AND SIGNIFICANCE

While statewide analysis is still being conducted some results are available. To date a total of 1441 horizons from 194 pedons have been sub-sampled for Hg analysis by a Direct Mercury Analyzer from Milestone Inc (model DMA-80). Samples were determined by availability and spatial distribution. Sampled soil orders include pedons from 74 Inceptisols, 54 Alfisols, 64 Ultisols, 2 Entisols, 1 Spodosol, and 1 Mollisol. Of these horizons, 975 have been analyzed thus far. Subsoil total Hg contents range from 10.7 to 470 ng/g; the highest surface horizon value found was 420 ng/g. Pedons sub-sampled for this study were initially sampled across the state in a time frame ranging from 1957-1984 (Figure 3).



A regional analysis has been completed on a local watershed at Black Moshannon Lake. In this sub-study total Hg sequestration appears to be greater in upland soils where both the surface horizon and subsurface horizons retain Hg. The Cookport soil series has the greatest total Hg pool, and generally does not border Black Moshannon Lake or areas with water tables less than 50 cm. However, this observation bodes poorly for the health of Black Moshannon Lake because the smaller pool of total Hg in the Nolo series and subaqueous soils in the lake is likely due to subsurface transport from the Cookport to the Nolo, and a loss of Hg from subaqueous soil Oe horizons via methylation. Though the Nolo series retained some total Hg in the surface horizon, both content and pools were low in subaqueous soils. This indicates that drainage and the downslope redirection of subsurface flow by a fragipan are two key controls on Hg transport.

Above a fragipan, redoximorphic features (RMFs) were found to be present, with Fe and Mn mineralogies and associated soil organic carbon (SOC) that can tightly bind Hg. In Black Moshannon Lake soils, the pattern between RMFs, SOC, and Hg distribution is still unclear, but it appears that RMFs may be short-term micro sinks and long-term source with intermittent saturation via water table fluctuation. The surface and subsurface Hg that is delivered to the subaqueous soil profile is likely very quickly lost with particulate matter or by chemical transformation. Black Moshannon Lake appears to be an environment in which Hg methylation is likely to occur. Since the Cookport series has the greatest total Hg pool, limiting disturbance in the Cookport series will perhaps limit Hg transport. Better infiltration to improve soil drainage in the Nolo soils may reduce methylation and subsurface transport to SASs. However, increased drainage will limit carbon sequestration potential, and perhaps upset the balance of the Black Moshannon Lake wetland system.



Soil organic carbon and Hg were not always correlated in transport and accumulation (as was seen in the subaqueous soil surface horizon, where the SOC pool was the greatest, but the total Hg pool was small). This suggests that management for carbon sequestration is possible without total Hg sequestration. However, the lack of a clear relationship makes predicting the distribution of total Hg based on SOC unreliable. Therefore a combination of other factors must be considered such as particle size, other complexing mineralogies, vegetation type and the resultant type of soil organic matter. Results suggest that Hg transport increases with increased wetness (based on a decrease in total Hg and previously established methylation in such environments), and is perhaps controlled by overland particle and organic matter transport, and subsurface transport across a fragipan to a more poorly drained soil. Subaqueous soils, because of their inundated state, provide an excellent environment for methylation. Understanding SOC and Hg sequestration, and the controls on those processes, can now be integrated with soil cartographic representations of the Black Moshannon Lake hydrosequence resulting in a useful management tool.

#### **STUDENTS & POSTDOCS SUPPORTED**

Emilie Erich, Soil Science, M.S.

#### **PHOTOS OF PROJECT**



Emilie Erich (foreground) and Mary Kay Lupton mapping subaqueous soils at Black Moshannon Lake. Photo, Patrick Drohan.



Patrick Drohan holding a soil core used to describe subaqueous soils in Black Moshannon Lake. Photo, Patrick Drohan.

# Coupled Analytical and Biological Analyses of Endocrine Disrupting Compounds (EDCs) of Emerging Concern in Municipal Wastewater Sources in Philadelphia

## Basic Information

<b>Title:</b>	Coupled Analytical and Biological Analyses of Endocrine Disrupting Compounds (EDCs) of Emerging Concern in Municipal Wastewater Sources in Philadelphia
<b>Project Number:</b>	2010PA141B
<b>Start Date:</b>	3/1/2010
<b>End Date:</b>	2/28/2011
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	1st and 2nd
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Water Quality, None, None
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	, Mohan Achary

## Publication

1. Johnson, M. Candice., Mohan P. Achary and Rominder P. Suri (in preparation). Estimating the Relative Estrogenic Potential using a Combined Experiment Approach . Environmental Toxicology and Chemistry Journal, submitted.

## **PROJECT TITLE & PRINCIPAL INVESTIGATORS**

### Coupled Analytical and Biological Analysis of Endocrine Disrupting Compounds (EDCs) of Emerging Concern in Municipal Wastewater Sources in Philadelphia

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## **PROBLEM & RESEARCH OBJECTIVES**

Endocrine disrupting activity has been detected in wastewater effluents of several water treatment facilities; thereby, conferring estrogenicity to receiving waters [1]. Evidence suggests that these hormones result in undesired characteristics to aquatic life even in the low ng/L range [2]. This is particularly because of the vast number of estrogens (of both natural and synthetic origin) that are combined in the complex wastewater matrix. Sophisticated analytical techniques allow the determination of the micro-constituents which may exist in the water. However, the biological activity of the wastewater matrix is best determined through the use of bioassays. Additionally, through the combined use of bioassays and analytical techniques any possible interaction amongst the components can be identified and discerned.

Proposed objectives:

- A. Determination of the concentrations of estrogens present in the influent and effluent samples of 3 WWTPs of Philadelphia using LC/MS/MS and LC Q-TOF-Mass Spectrometry
- B. Effect directed analyses of wastewater derived estrogens using the E-Screen and the Yeast Estrogen Screen

To achieve the objectives of this study we focused on the following specific aims:

- 1) Determining the concentrations of target estrogens in the wastewater sample.
- 2) Determining whether or not an interaction occurs amongst the hormones in the wastewater matrix.
- 3) Predicting the biological activity of the influent and effluent samples based on chemical data.

## **METHODOLOGY**

The techniques used include the Yeast Estrogen Screen (YES) assay and the E-Screen assay which utilizes estrogen receptor positive MCF-7 cells as representative bioassays for the determination of estrogenicity, and Liquid chromatography tandem mass spectroscopy (LC-MS/MS) for the quantification of hormones present in the samples.

### ***LC-MS/MS***

These instruments offer superb sensitivity and resolution for analyte detection. Estrogen hormones are extracted from the wastewater samples using Solid Phase Extraction (SPE). This allowed for the detection of analytes that are present in the ng/L range by concentration of the sample. We followed the methods that are already established for the detection of estrogen hormones in the analytical laboratory of Dr. Suri, the Co-PI in this project.

### ***Water Collection and Estrogen Extraction***

Grab wastewater influent and effluent samples were collected from a local municipal wastewater treatment works facility and stored in amber glass bottles. The facility serves 9 municipalities, 2 hospitals, and receives 60% of its water from municipal and 40% industrial sources. Secondary treatment is achieved using the activated sludge process. Within 24 hours after water collection samples were vacuum filtered through a 0.45 $\mu$ m membrane in preparation for solid phase extraction (SPE) of the estrogens. SPE was performed on a C-18 cartridge (Varian BondElute) under gentle vacuum. Samples were eluted in 6 mL of methanol after pre-cleaning with 6mL of 30% methanol in water. This served to reduce matrix interferences which may hinder analytical detection. Eluents were dried under vacuum and reconstituted in a 50% methanol/water solution for detection on UPLC-MS/MS. Influent and effluent samples were enriched 500 and 750 times for analytical detection and 4900 and 7400 times respectively for biological assays. In preparation for biological analysis, dried eluents were reconstituted in pure ethanol.

### ***Yeast Estrogen Screen (YES) Assay***

The YES was carried out as per the Routledge and Sumpter method [3]. This assay makes use of a modified strain of yeast developed by Routledge and Sumpter and provided by Dr. Joseph Colosi of De Sales University. In order to construct this recombinant strain, the human cDNA sequence coding for the ER (hER) was integrated into the genome of the yeast *Saccharomyces cerevisiae*, under the control of a yeast promoter. The yeast also contained a plasmid carrying an ERE-LacZ construct controlling the oestrogen-induced expression of the reporter gene *LacZ*, encoding the enzyme b-galactosidase. Thus, in the presence of estrogen the yeast synthesizes b-galactosidase, which splits the yellow chromogenic substrate chlorophenol red- $\beta$ -D-galactopyranoside (CPRG), present in the assay-medium, into galactose and the chromophore chlorophenol red, yielding a dark red compound. The b-galactosidase activity is quantified spectrophotometrically at 540nm [3].

Stock solutions of 17 $\beta$ -Estradiol, Estriol, 17 $\alpha$ -Dihydroequilin, and Estrone were prepared in ethanol and stored at -20C. Mixtures of the above compounds were prepared by transferring a relevant amount of a single solution onto a flat bottom 96 well plate and allowing the ethanol to evaporate to dryness before adding the other mixture constituents. Assay medium (comprising of yeast at a final optical density (OD) of 0.1, CPRG, and growth medium) were then added to the well. The plate was then incubated for 72 hours at 32°C. The conversion of chlorophenol red- $\beta$ -D-galactopyranoside (CPRG) to chlorophenol red (CPR) was measured by recording absorbance values at 540nm and correcting for yeast growth at 630nm. Similarly, 5-10 $\mu$ L of the extracted samples were placed in the plates and allowed to dry prior to the addition of assay medium. The relative estrogenic potential (REP) of the extracts was used as a measure of estrogenicity. In case of the extracts the biological response is plotted against the relative enrichment factor (REF)

which represents the final concentration factor if the extract to which the biological organism was exposed. The REF is calculated as [4]:

$$REF = \left( \frac{V_{estrogens}}{V_{extract}} \right) \bullet \left( \frac{V_{extract}^{bioassay}}{V_{bioassay}} \right); \text{ where } V \text{ represents the volume of the respective samples.}$$

Without statistical evidence of parallelism amongst the dose response curves, multipoint estimates of the REP were determined at the EC10, EC20, EC50, and EC80 levels when possible. Percent reductions in estrogenicity were then calculated at each effect level then averaged to yield a single estimate in reductions.

### ***E-Screen (ES) Assay***

The E-Screen utilizes the proliferative ability of estrogen positive MCF-7 breast cancer cells [5]. The MCF-7-BUS cells used in our study were received from the laboratory of Dr. Ana Soto of Tufts University. These cells were used as they are sensitive and can produce a response that is approximately six times than that of original MCF-7 cell line. The assay is based on the fact that MCF-7 cells naturally express the estrogen receptor isoforms and undergo increased growth rates as a result of the activation of the estrogen receptor. The experimental conditions involve seeding cells under estrogen free conditions; that is, in growth medium without phenol red and with Charcoal-dextran stripped fetal bovine serum. The stripping of the serum removes any compounds which may inhibit the response to estrogens.

The cells were routinely maintained in DMEM supplemented with 2% HEPES, 2% Glutamine, 1% Penn/strep, and 10% FBS. Experimental medium contained phenol-red free DMEM supplemented with HEPES, Glutamine, and Penn/strep as above in addition to 10% charcoal stripped FBS. Stock solutions were prepared in ethanol and diluted in experimental medium such that the final ethanol concentration did not exceed 0.1%. Cells were seeded into 6-well plates at an initial density of 50,000 cells / well and allowed to attach. After 24 hours, medium containing the test compounds was added and cells incubated for 6 days. Following incubation, the cells were trypsinized and counted using a TC Biorad automatic cell counter. The estrogenic activity was quantified as the relative proliferative effect (RPE). This is simply the ratio of the highest cell yield obtained with the test substance and estradiol, and is calculated as

$$RPE = 100 \times \frac{PE_{test} - 1}{PE_{estradiol} - 1}$$

### ***Modeling biological activity***

Initial studies focused on determining the interactive potential of the hormones found at wastewater treatment when combined. The biological activity of the mixtures was analyzed using the YES. The concentration addition (CA) model was also used to investigate the additivity of specified mixtures [6-8]. In brief, the CA assumes that each mixture constituent acts as a dilution of the other, with the relative estrogenic potential (REP) of the compound serving as the dilution factor [9]. Deviations from additivity are then easily discerned as variation of the observed biological responses to the predicted outcome. The model is derived and utilized as follows;

For a binary mixture an interaction can be defined by Equation 1 [6, 10,11].

$$\frac{C_1}{EC_{x,C_1}} + \frac{C_2}{EC_{x,C_2}} = I \quad (1)$$

where ‘I’ represents the interactive index,  $C_i$  is the concentration of compound  $C$  in the mixture exerting an  $EC_x$  effect and  $EC_{xi}$  represents the equal effect concentration of  $C$  alone.

If compounds 1 and 2 act additively then ‘I’ is equal to unity. An interaction is then defined as I assuming a value greater than 1 for synergistic activity or less than 1 for antagonism. The equation can be rearranged in terms of the total mixture concentration,  $C_T$ , and the proportion of each mixture constituent,  $P_x$ . Thus, given a fixed ratio design the following is true if additivity is assumed.

$$C_T \left[ \frac{P_1}{EC_{x,C_1}} + \frac{P_2}{EC_{x,C_2}} \right] = 1, \quad (2)$$

Equation 2 allows for the prediction of the mixture response based on the proportion of the mixture components and the standalone response of each individual component. Rearrangement gives the working formula, equation 3.

$$C_T = \left[ \sum \frac{P_i}{EC_{x,C_i}} \right]^{-1} \quad (3)$$

## PRINCIPAL FINDINGS AND SIGNIFICANCE

### LC-MS/MS determination of estrogens in wastewater

Table 1 shows the concentrations of natural estrogens found in wastewater treatment plant influent and effluent determined from the calibration curves shown in Figure 1. It appeared that 17 $\beta$ -estradiol was significantly removed in the treatment process whereas estriol and 17 $\alpha$ -dihydroequilin was removed to a lesser extent, 24 and 54% respectively. Estrone on the other hand appeared to increase in the wastewater effluent by approximately 77%. This result agrees with previously published reports of metabolic conversion of 17 $\beta$ -estradiol to estrone in the activated sludge process [12-14]. As such, estrone is often viewed as one of the hormones primarily responsible for endocrine disruption in aquatic species [15].

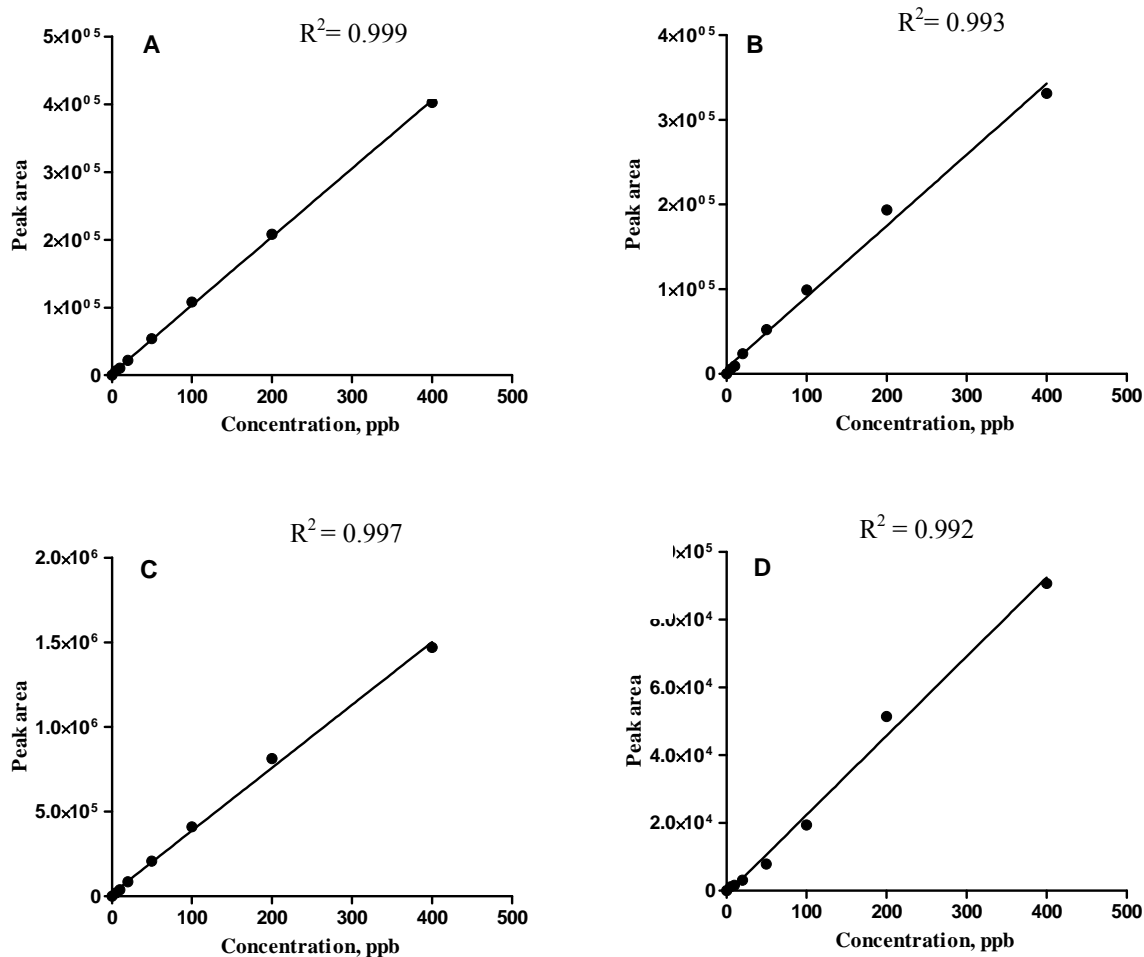


Figure 1- Calibration curves for A) estriol, B) 17 $\beta$ -estradiol, C) estrone, D) 17 $\alpha$ -dihydroequilin after SPE and determined using LC-MS/MS

Table 1- Concentration of estrogen hormones in the influent and effluent of the water treatment facility

	Estriol	17 $\beta$ -estradiol	estrone	17 $\alpha$ -dihydroequilin
Influent (ng/L)	8.66	5.07	0.15	679.18
Effluent (ng/L)	6.55	*ND	0.65	311.61
% Reductions	24.35	100	**N/A	54.12

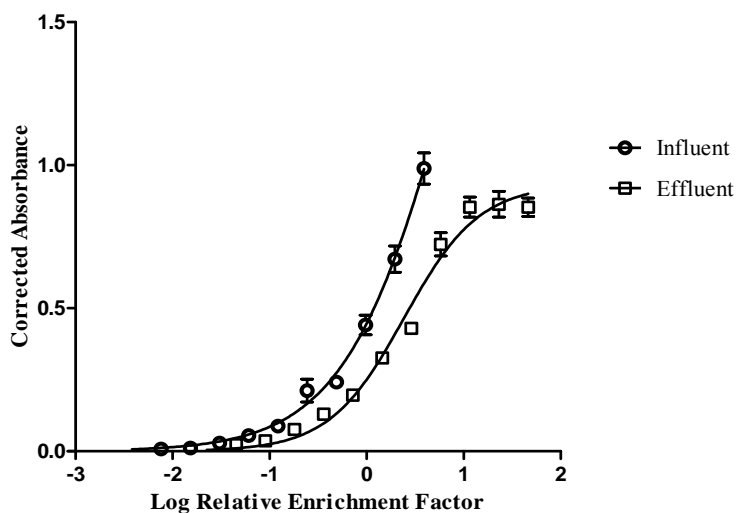
\* Not detected

\*\* An increase in final effluent concentration is observed



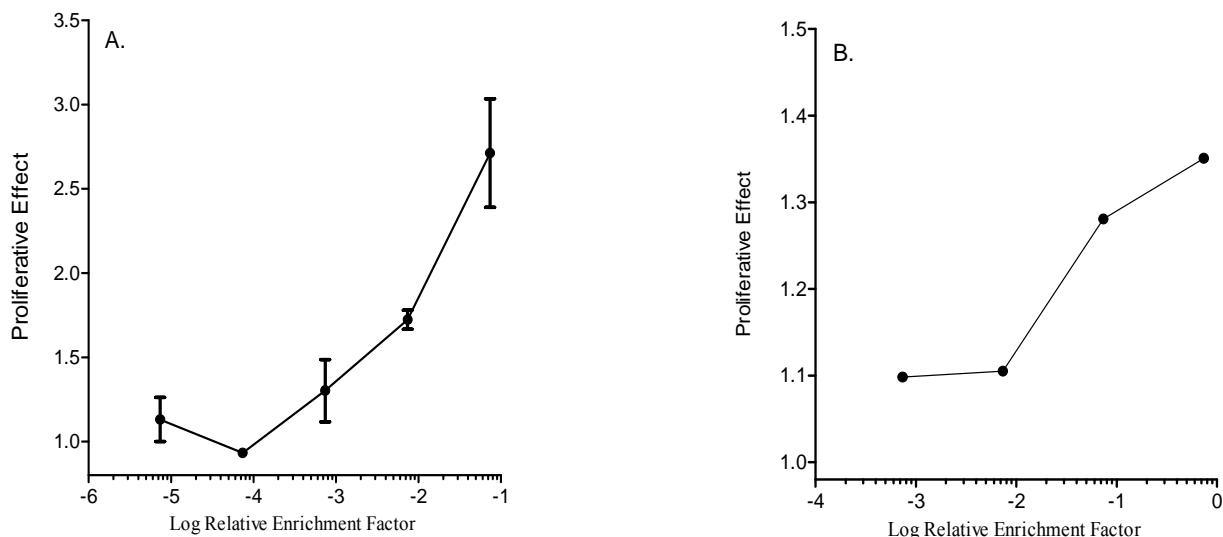
## Biological activity of influent and effluent assessed using YES and E-screen

As expected from the chemical data above, the wastewater effluent contained significant residual activity in spite of treatment. In order to quantify the changes in the estrogenic activity observed without confirmation of parallelism to the standard  $17\beta$ -estradiol, the relative estrogenic potential (REP) was calculated at several effect levels and averaged. The residual activity of the effluent was 61% less than that of the influent reflecting the incomplete degradation of the hormones investigated (Figure 2). Similar reductions in the proliferative effect of the influent and effluent samples were observed with the E-screen assay which showed approximately 79.5% reduction in estrogenic activity. The effluent samples also yielded a submaximal response in the E-screen assay and a full dose response curve was not achieved in the influent samples due to the toxic effect, Figure 3.



Effect Level (%)	Influent REP	Effluent REP	% Reduction
80	0.0206	N/D	N/D
50	0.0193	0.00751	61.1
20	0.0307	0.0131	57.5
10	0.0467	0.0164	64.8
		Average	61.1

Figure 2- Dose response curves and percent reductions in the estrogenicity of influent and effluent samples



	Influent	*Effluent	% Reduction in RPE
Relative proliferative effect (RPE)	39.8	8.16	79.5

\*Pending replication of these experiments

Figure 3- A. influent, and B. effluent sample responses in the E-screen assay. The highest concentration tested in both samples was toxic to the cells as determined by microscopic observation.

### Comparison of chemical and biological estradiol equivalents in YES

The chemically determined concentrations were converted into expected biological responses using the CA model described above. The predictions were made based on the single compound dose response curves shown in figure 4. Laboratory prepared mixtures of  $17\beta$ -estradiol, estriol, estrone, and  $17\alpha$ -dihydroequilin showed that there was no expected interaction amongst the hormones as the response could be predicted within the 95% confidence interval of the observed response, figure 5. In the case of the wastewater samples, the predicted enrichment factors were calculated through the division of the total mixture concentration determined by the model by the summed concentration determined by LC-MS/MS. The CA model roughly predicted the responses up to about the  $EC_{10}$  in both cases; thereafter, deviations from additivity were observed. This appears to arise as a result of dissimilar hill slopes in the case of both the influent and effluent samples. The submaximal effluent curve was also not predicted by the model. Since an interaction is not expected based on a simulation of the mixture composition in ethanol, it is hypothesized that this deviation may result from either the effect of unknown components such as humic acids, or a decrease in enzyme activity associated with the wastewater matrix. Of interest however, is the fact that the reduction in estrogenicity determined by the chemical analysis (61.5%) is in good agreement with that determined by the bioassay.

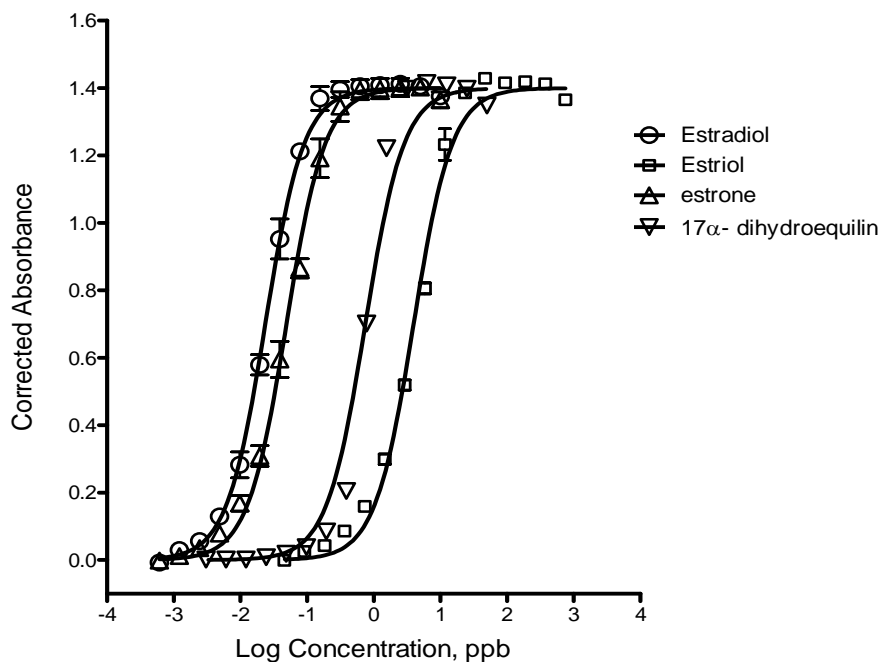


Figure 4- Single compound analysis in the YES assay.

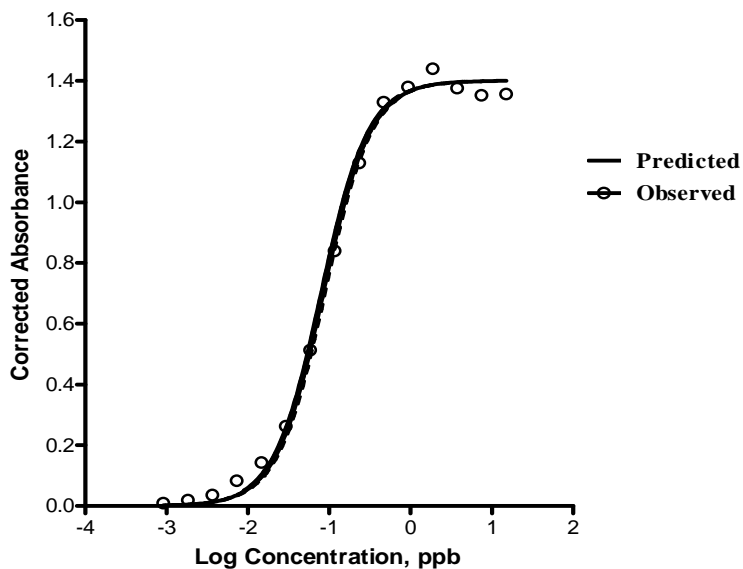


Figure 5. 17 $\beta$ -estradiol, estriol, estrone, and 17 $\alpha$ -dihydroequilin were combined and the CA model used to predict the responses. The observed responses were well predicted by the model indicating that there is no potential for an interaction amongst these hormones.

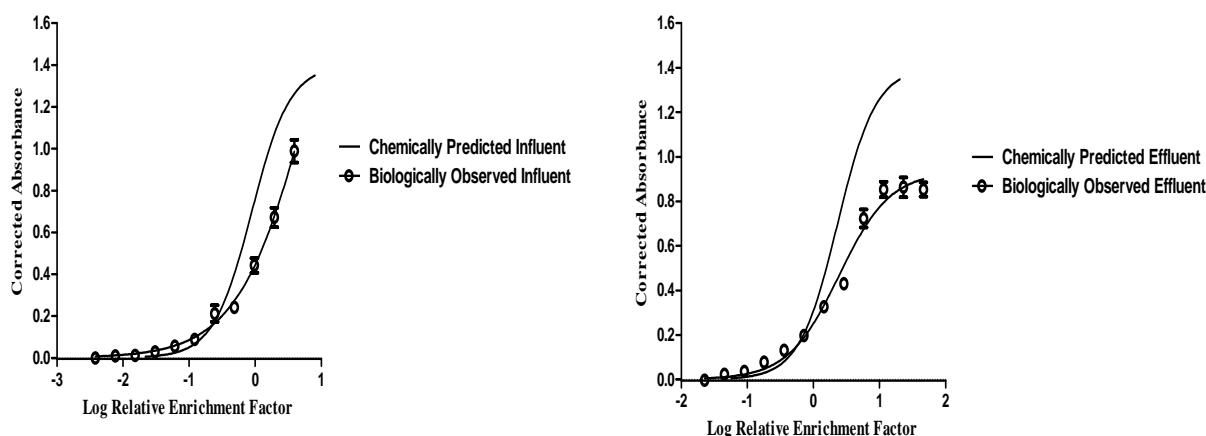


Figure 6. Calculated and observed dose response curves for all effect levels of the influent and effluent samples in the yeast estrogen screen (YES) assay. An antagonistic-like activity was observed in both the wastewater influent and effluent samples.

Future studies will include testing recoveries in wastewater matrix by spiking with a labeled internal standard and assessment of additional treatment facilities during both winter and summer seasons to assess the variability in the degradation patterns which may occur.

#### STUDENTS & POSTDOCS SUPPORTED (name, major, degree)

1. Ms. Candice Johnson, MS: Doctoral student
2. Mr. Benjamin Conway, BS: Graduate student

Both Ms. Johnson and Mr. Conway assisted Dr. Achary in achieving the results provided in this report.

**Note:** For additional information please visit, [www.hdcsetac.org](http://www.hdcsetac.org)

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# **Information Transfer Program Introduction**

None.

# Public Education on Water Issues Related to Marcellus Gas Drilling

## Basic Information

<b>Title:</b>	Public Education on Water Issues Related to Marcellus Gas Drilling
<b>Project Number:</b>	2010PA121B
<b>Start Date:</b>	3/1/2010
<b>End Date:</b>	2/28/2011
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	PA-005
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Education, None, None
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Bryan Reed Swistock

## Publications

1. Abdalla, C, J. Drohan, B. Swistock, and S. Boser. 2011. Marcellus Shale Gas Well Drilling: Regulations to Protect Water Supplies in Pennsylvania. Penn State Extension fact sheet, 6 pp. [http://extension.psu.edu/water/marcellus-shale/marcellus-shale-gas-well-drilling-regulationsto-protect-water-supplies-in-pennsylvania/at\\_download/file](http://extension.psu.edu/water/marcellus-shale/marcellus-shale-gas-well-drilling-regulationsto-protect-water-supplies-in-pennsylvania/at_download/file)
2. Abdalla, C., J. Drohan, K. Saacke Blunk, and J. Edson. Marcellus Shale Wastewater Issues in Pennsylvania—Current and Emerging Treatment and Disposal Technologies. 2011. Penn State Extension fact sheet, 9 pp. [http://extension.psu.edu/water/marcellus-shale/marcellusshale-wastewater-issues-in-pennsylvania-current-and-emerging-treatment-and-disposaltechnologies/at\\_download/file](http://extension.psu.edu/water/marcellus-shale/marcellusshale-wastewater-issues-in-pennsylvania-current-and-emerging-treatment-and-disposaltechnologies/at_download/file)
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## **PROJECT TITLE AND PRINCIPAL INVESTIGATORS**

Public Education on Water Issues Related to Marcellus Gas Drilling

Bryan R. Swistock, Charles Abdalla, Susan Boser, James Clark, Mark Madden, Thomas McCarty, Dana Rizzo, Scott Sjolander, and Peter Wulfhorst; Penn State Cooperative Extension

## **PROBLEMS AND RESEARCH OBJECTIVES**

New drilling technologies to reach previously untapped gas reserves in the Marcellus shale have resulted in expanded drilling of deep gas wells throughout much of Pennsylvania. Marcellus gas drilling is a more intensive process in comparison to traditional gas drilling that has been commonplace throughout western and northern Pennsylvania for many decades. The scale of Marcellus activity, both geographically and spatially, has created concerns related to the amount of water used, safety of hydrofracturing, disposal of waste fluids, and protection of streams, wetlands and drinking water supplies during the drilling process. The objective of this project was to organize a team of Penn State Extension field educators and specialists to deliver unbiased public education on water issues related to Marcellus gas drilling activities.

## **METHODOLOGY**

The project first built a team of water resources specialists and extension educators through a face-to-face training workshop in early 2010. The team then organized to create a series of written and web-based educational resources on various water issues related to Marcellus gas drilling. These resources were housed on a new web site and were also used to deliver numerous face-to-face and online workshops for various stakeholder groups throughout the Marcellus region. Evaluations were used to document impacts from these educational efforts.

## **PRINCIPAL FINDINGS AND SIGNIFICANCE**

Penn State Extension is recognized as a source of unbiased, factual information related to Marcellus gas drilling. This project resulted in the development of a cohesive, statewide team of nine Extension water specialists and county educators who can respond to current and future needs for public education on water resources issues Marcellus gas drilling. A web site was created to house the resources created by the group at: <http://extension.psu.edu/water/marcellus-shale>. The website currently receives about 1,500 visitors each month and is growing rapidly. This combination of a dedicated team of trained educators and extensive educational resources creates a strong, statewide effort to provide unbiased education on water issues related to Marcellus gas development. The attendance at workshops and evaluation data from participants demonstrate the strong public interest in this subject and the critical need for unbiased, factual information on the topic.

## **STUDENTS & POSTDOCS SUPPORTED**

- Michelle Cleveland, M.S. Ecology, 2010 – Michelle was employed on wages during the fall of 2010 to assist with publications and web site development.
- Shawn Rummel, Post Doc, PhD, Ecology, 2010 – Shawn was also briefly employed during the spring and summer of 2010 to assist with publications and video script preparation.



## **EXTENSION PUBLICATIONS**

Team members created a series of seven extension publications on critical water issues related to Marcellus gas drilling including:

1. Abdalla, C, J. Drohan, B. Swistock, and S. Boser. 2011. Marcellus Shale Gas Well Drilling: Regulations to Protect Water Supplies in Pennsylvania. Penn State Extension fact sheet, 6 pp. [http://extension.psu.edu/water/marcellus-shale/marcellus-shale-gas-well-drilling-regulations-to-protect-water-supplies-in-pennsylvania/at\\_download/file](http://extension.psu.edu/water/marcellus-shale/marcellus-shale-gas-well-drilling-regulations-to-protect-water-supplies-in-pennsylvania/at_download/file)
2. Abdalla, C., J. Drohan, K. Saacke Blunk, and J. Edson. Marcellus Shale Wastewater Issues in Pennsylvania—Current and Emerging Treatment and Disposal Technologies. 2011. Penn State Extension fact sheet, 9 pp. [http://extension.psu.edu/water/marcellus-shale/marcellus-shale-wastewater-issues-in-pennsylvania-current-and-emerging-treatment-and-disposal-technologies/at\\_download/file](http://extension.psu.edu/water/marcellus-shale/marcellus-shale-wastewater-issues-in-pennsylvania-current-and-emerging-treatment-and-disposal-technologies/at_download/file)
3. Sjolander, S., J. Clark, D. Rizzo and J. Turack. Introduction to Hydrofracturing. 2011. Penn State Extension fact sheet, 7 pp. [http://extension.psu.edu/water/marcellus-shale/introduction-to-hydrofracturing/at\\_download/file](http://extension.psu.edu/water/marcellus-shale/introduction-to-hydrofracturing/at_download/file)
4. Swistock, B. Testing Drinking Water Supplies Near Gas Drilling Activity. 2011. Penn State Extension fact sheet, 4 pp. [http://extension.psu.edu/water/marcellus-shale/testing-drinking-water-supplies-near-gas-drilling-activity/at\\_download/file](http://extension.psu.edu/water/marcellus-shale/testing-drinking-water-supplies-near-gas-drilling-activity/at_download/file)
5. Abdalla, C. J. Drohan, and J. Becker. 2010. River Basin Approaches to Water Management in the Mid-Atlantic States, Penn State Extension publication UA466, 28 pp. <http://pubs.cas.psu.edu/FreePubs/pdfs/ua466.pdf>
6. Swistock, B. 2010. Chain of Custody Water Testing, Penn State Extension fact sheet, 3 pp. [http://extension.psu.edu/water/marcellus-shale/thirdpartylabs.pdf/at\\_download/file](http://extension.psu.edu/water/marcellus-shale/thirdpartylabs.pdf/at_download/file)
7. Abdalla, C. and J. Drohan. 2010. Water Withdrawals for Development of Marcellus Shale Gas in Pennsylvania, Penn State Extension publication UA460, 12 pp. [http://extension.psu.edu/water/resources/publications/consumption-and-usage/marcelluswater.pdf/at\\_download/file](http://extension.psu.edu/water/resources/publications/consumption-and-usage/marcelluswater.pdf/at_download/file)

## **PRESENTATIONS AND OTHER INFORMATION TRANSFER ACTIVITIES**

The project team utilized the various resources developed in this project to present 46 educational programs or webinars in 21 counties throughout the Marcellus region of the state. These programs were attended by over 3,500 participants including water supply owners, legislators, local government officials, farmers, researchers, and water resources professionals. Topics of workshops included general water issues related to Marcellus gas drilling, protecting private drinking water supplies, interpreting water test reports, and strategies to treat or dispose of drilling wastewaters. Dates, location, topics and attendees (in parentheses) for each workshop are listed below:

1. 3/1/2010, State College, PA, Water Resources Issues Related to Natural Gas Drilling (95)
2. 3/5/2010, Dimock, PA, Gas Well Drilling and Private Water Supplies (63)
3. 3/10/2010, Harrisburg, PA, Water Resources Issues Related to Natural Gas Drilling (22)

4. 3/20/2010, State College, PA, Water Resources Issues Related to Natural Gas Drilling (80)
5. 3/23/2010, State College, PA, Water Resources Issues Related to Natural Gas Drilling (68)
6. 4/20/2010, Hershey, PA, Water Resources Issues Related to Natural Gas Drilling (102)
7. 5/4/2010, State College, PA, Water Resources Issues Related to Natural Gas Drilling (12)
8. 5/12/2010, Wyalusing, PA, Gas Well Drilling and Private Water Supplies (115)
9. 5/13/2010, Lake Lehman, PA, Gas Well Drilling and Private Water Supplies (137)
10. 5/17/2010, Renovo, PA, Water Resources Issues Related to Natural Gas Drilling (6)
11. 5/20/2010, New Castle, PA, Water Resources Issues Related to Natural Gas Drilling (135)
12. 6/1/2010, Pittsburgh, PA, Water Resources Issues Related to Natural Gas Drilling, (100)
13. 6/9/2010, State College, PA, Water Resources Issues Related to Natural Gas Drilling (22)
14. 6/10/2010, Waynesburg, PA, Water Resources Issues Related to Natural Gas Drilling (33)
15. 6/14/2010, State College, PA, Wastewater Reuse and Recycling for Marcellus Gas Drilling (51)
16. 6/15/2010, Honesdale, Gas Well Drilling and Private Water Supplies, (90)
17. 6/21/2010, Clarion, PA, Water Resources Issues Related to Natural Gas Drilling (210)
18. 6/22/2010, Ford City, PA, Water Resources Issues Related to Natural Gas Drilling (140)
19. 7/20/2010, Lancaster, PA, Water Testing Near Marcellus Gas Drilling (36)
20. 7/26/2010, Wysox, PA, Water Resources Issues Related to Natural Gas Drilling (47)
21. 8/5/2010, Wysox, PA, Interpreting Pre and Post Gas Drilling Water Test Reports (220)
22. 8/11/2010, Dimock, PA, Interpreting Pre and Post Gas Drilling Water Test Reports (139)
23. 8/17/2010, Rock Springs, PA, Gas Well Drilling and Private Water Supplies (42)
24. 8/18/2010, Rock Springs, PA, Gas Well Drilling and Private Water Supplies (47)
25. 8/19/2010, Clarion, PA, Water Resources Issues Related to Natural Gas Drilling (110)
26. 8/19/2010, Rock Springs, PA, Gas Well Drilling and Private Water Supplies (29)
27. 8/23/2010, Wysox, PA, Interpreting Pre and Post Gas Drilling Water Test Reports (60)
28. 9/14/2010, Wellsboro, PA, Interpreting Pre and Post Gas Drilling Water Test Reports (76)
29. 9/15/2010, Statewide webinar, Interpreting Pre and Post Gas Drilling Water Test Reports (57)
30. 9/24/2010, University Park, PA, Water Resources Issues Related to Natural Gas Drilling (52)
31. 9/27/2010, Lehman, PA, Interpreting Pre and Post Gas Drilling Water Test Reports (43)
32. 9/29/2010, Baltimore, MD, Water Resources Issues Related to Natural Gas Drilling (104)
33. 10/13/2010, State College, PA, Gas Well Drilling and Private Water Supplies (75)
34. 10/19/2010, Tunkhannock, PA, Interpreting Pre and Post Gas Drilling Water Test Reports (76)
35. 10/27/2010, Statewide webinar, Water Resources Issues Related to Natural Gas Drilling (32)
36. 12/1/2010, Ebensburg, PA, Water Resources Issues Related to Natural Gas Drilling (53)
37. 12/14/2010, State College, PA, Water Resources Issues Related to Natural Gas Drilling (18)
38. 12/14/2010, Scranton, PA, Gas Well Drilling and Private Water Supplies, (40)
39. 12/15/2010, Johnstown, PA, Water Resources Issues Related to Natural Gas Drilling (53)

40. 12/16/2010, Venango County, PA, Water Resources Issues Related to Natural Gas Drilling (150)
41. 12/16/2010, Clarion, PA, Water Resources Issues Related to Natural Gas Drilling (80)
42. 1/28/2011, Grantville, PA, Gas Well Drilling and Private Water Supplies (210)
43. 2/3/2011, Coudersport, PA, Interpreting Pre and Post Gas Drilling Water Test Reports (48)
44. 2/9/2011, Trout Run, PA, Gas Well Drilling and Private Water Supplies (20)
45. 2/16/2011, Baltimore, MD, Water Resources Issues Related to Natural Gas Drilling (131)
46. 2/21/2011, Canton, PA, Gas Well Drilling and Private Water Supplies (22)

Approximately 1,200 of the 3,550 attendees at these workshops completed and returned a workshop evaluation. Results of these evaluations showed that:

- 92% planned to use the information to better manage and protect their water resources near gas drilling activity and
- 85% felt that the information presented was unbiased and factual

A follow-up evaluation of attendees found that 87% had taken a recommended action to protect water resources near gas drilling. Some of the most common actions reported were:

- Using DEP tools to learn about gas well locations (26%)
- Stipulate water protection strategies in a subsequent gas lease (8%)
- Have drinking water tested by a state accredited water lab before drilling (20%)
- Purchase a TDS meter to monitor water during drilling (5%)
- Have water quantity documented by a water well contractor or hydrogeologist (5%)

A short (8-minute) web-based video was produced by a professional videographer (Christopher Fagan, State College, PA) for use in online programs and by team members. The video discusses basic water issues related to Marcellus gas drilling. A draft of the video currently resides on YouTube at <http://www.youtube.com/watch?v=jWmiLUPKHIE>. The video will also be linked to the Penn State Water Resources Extension website and hardcopies will be distributed to team members for use in educational programs.

## **AWARDS**

The investigators on the project received the Penn State Extension, Team Award at the Extension Annual Conference in Altoona, PA in November, 2010 for their work on the Extension Safe Drinking Water Team. Much of this award was related to programs developed as a result of this project for private water system owners in the Marcellus region of the state.

## **ADDITIONAL FUNDING ACQUIRED USING USGS GRANT AS SEED MONEY**

None

## PHOTOS OF PROJECT



Water Resources Extension educator Peter Wulfhorst (background) and specialist Bryan Swistock (foreground) assist several homeowners with interpretation of pre gas drilling water test reports.



Water Resources Extension Specialist Bryan Swistock discusses regulations to protect drinking water supplies from gas drilling activity with approximately 100 homeowners in Tunkhannock, PA.

# Pennsylvania Water Resources Research Symposium

## Basic Information

<b>Title:</b>	Pennsylvania Water Resources Research Symposium
<b>Project Number:</b>	2010PA126B
<b>Start Date:</b>	3/1/2010
<b>End Date:</b>	2/28/2011
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	PA-005
<b>Research Category:</b>	Ground-water Flow and Transport
<b>Focus Category:</b>	Water Quality, Water Quantity, Water Use
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Elizabeth Boyer, Bryan Reed Swistock

## Publications

There are no publications.

## **PROJECT TITLE & PRINCIPAL INVESTIGATORS**

Pennsylvania Water Resources Research Symposium

Elizabeth W. Boyer and Bryan R. Swistock, School of Forest Resources, Pennsylvania State University

## **PROBLEM & RESEARCH OBJECTIVES**

Concerns over water resources have been growing in Pennsylvania in recent years, in response to severe droughts and floods, a growing population, increasing demands for water, pressing issues at the water-energy nexus, and the need to understand how changes in land use and climate will affect water quantity and quality.

The Pennsylvania Water Resources Research Institute aims to host a symposium on water resources research in Pennsylvania. This symposium will promote exchange among researchers and others interested from academia, government, industry, environmental, and public interest groups. The symposium intends to provide a venue to foster information sharing and idea development among researchers, and to consider the role of research in advancing understanding of water quality and water quantity issues in Pennsylvania.

## **METHODOLOGY**

A planning committee was formed to organize and plan the Symposium, consisting of Elizabeth Boyer (Director, Pennsylvania Water Resources Research Center), Bryan Swistock (State Water Extension Specialist, Pennsylvania State University), Pat Bowling and Joe Lee (Source Water Protection, the Pennsylvania Department of Environmental Protection), and Stephanie Clemons (Pennsylvania Master Well Owner Network).

The committee contributed to fund raising toward offsetting costs of participant registration fees (and more), and secured contributions from the Pennsylvania Department of Environmental Protection, the Penn State Master Well Owner Network, the Penn State Environmental & Natural Resources Institute, the Penn State Earth & Environmental Systems Institute, and the Pennsylvania Ground Water Association. The primary sponsor was the Pennsylvania Water Research Center.

The meeting was advertised state-wide, through email, electronic list-servs and in various publications. Abstracts were solicited for both oral and poster presentations, and the planning committee formed the conference agenda.

## **PRINCIPAL FINDINGS AND SIGNIFICANCE**

The Pennsylvania Water Symposium was held at the Penn Stater Conference Center on May 5-6 2010.

There were 200 participants from a wide range of institutions, including:

- (30) NGOs, Water Associations, & Watershed Groups.

- (29) Consultants.

- (11) Regional Agencies (Conservation Districts, Planning Commissions, Interstate River Basin Commissions, County Government officers).

- (52) State Agencies (PADEP, PAGS, USGS, USDA, USEPA).

- (12) Cooperative extension educators and agents.

- (66) Faculty & Students from Colleges, Universities, Research Centers (representing 17 institutions).

Keynote speakers included John Hines, the Deputy Secretary for Water Management, Pennsylvania Dept. of Environmental Protection; and Jerad Bales, the Chief Scientist for Hydrology, US Geological Survey, Reston, VA. Oral presentations were held in the areas of Watershed Processes & Management (5 presentations), Applied Ground Water (5 presentations), Contemporary Water Issues and Potential Solutions (5 talks). In addition, meeting participants contributed over 30 poster presentations.

The meeting was assessed by Penn State's Office of Conferences and Short Courses, and was generally well-received. The Pennsylvania Water Resources Research Center hopes to sponsor similar events in the future.

The full symposium agenda is below.

**Pennsylvania Water Symposium**  
***Theme: Ground Water & Surface Water – A Single Resource***  
May 5-6, 2010, Penn Stater Conference Center Hotel, State College, PA

**May 5, 2010**

**6:00 pm - 8:00 pm, Reception.** (Included with registration). Learn who's who in Pennsylvania water. Join us for hors d'oeuvres and refreshments; cash bar will be available. *Posters may be hung anytime during the reception. Velcro will be provided at the registration desk.*

**May 6, 2010**

**7:30 – 8:30, Registration.** Come early. *Posters may be hung anytime during registration.*

**8:30 – 9:30, Priorities for Pennsylvania: An Overview of Key Issues.**

- (8:30-8:40) *Welcome and Introductory Remarks.* **Bryan Swistock** (Pennsylvania State Water Extension Specialist, Pennsylvania State University) and **Elizabeth Boyer** (Director, Pennsylvania Water Resources Research Center).
- (8:40-9:00). *Current Issues in Water Management in Pennsylvania.* Keynote speaker **John Hines** (Deputy Secretary for Water Management, Pennsylvania Dept. of Environmental Protection).
- (9:00-9:20). *Water Resources for Pennsylvania and the Nation.* Keynote speaker **Jerad Bales** (Chief Scientist for Hydrology, US Geological Survey, Reston, VA).

**9:25 – 10:25, Poster Session.** *Poster Presentations* contributed by meeting participants.

**10:25 – 12:00, Watershed Processes & Management.** Session moderator: **Sarah Whitney** (Pennsylvania Sea Grant, Harrisburg, PA).

- (10:25-10:40) *Advances in Understanding Watershed Processes with Real-time in-Situ Sensor Networks for Surface and Ground Water Properties.* **Anthony Aufdenkampe** (Assistant Research Scientist, Stroud Water Research Center).
- (10:45-11:00) *Should the Clean Water Act Follow Stream Water Underground? Managing What We Can't See in the Hyporheic Zone.* **Mike Gooseff** (Assistant Professor, Dept. of Environmental Engineering, Penn State University).
- (11:05-11:20) *Nitrogen, Phosphorus, and Sediment Dynamics at Big Spring Run: A Case Study for a New Floodplain-Wetland Stream Restoration Management Plan.* **Robert Walter** (Franklin & Marshall), Dorothy Merritts (F&M), Yupu Zhao, (F&M), Chris Fullinwider (F&M), Mike Rahnis (F&M), Paul Mayer (EPA), Ken Forshay (EPA), Mike Langland (USGS), Allen Gellis (USGS), Jeff Hartranft (PA DEP), and Ward Oberholtzer (LandStudies).
- (11:25-11:40) *Plan B(asin): It's Not Just the Bay Anymore.* **Denice Wardrop** (Chair, Chesapeake Bay Program's Scientific and Technical Advisory Committee).
- (11:45-12:00). *Ground Water Monitoring and Source Protection in Pennsylvania.* **Joe Lee** (Chief, Source Water Protection, Pennsylvania Department of Environmental Protection).

**12:00– 1:00 Lunch** (included with registration).



**1:00 – 2:50 Applied Ground Water Resources.** Session moderator: **Patrick Bowling** (Pennsylvania Department of Environmental Protection)

- (1:00-1:15). *Source Water Protection in the Lehigh Valley: The Challenges of Determining Surface and Ground Water Flow in a Karst Valley.* **Alfred Guiseppe** (Geologist, SSM Group).
- (1:20-1:35). *Protecting Groundwater Quality: The Spring Creek Watershed Drilling Ordinance Success Story.* **Todd Giddings** (President, Todd Giddings & Associates).
- (1:40-1:55). *Completion, Testing and Permitting of a 2.1 MGD Municipal Water Supply Well in the South Mountain Physiographic Province, Franklin County, Pennsylvania.* **Bill Seaton** (Senior Hydrogeologist, ARM Group).

**2:00-2:15, Break.**

- (2:15-2:30). *Evaluation of Base Flow and Impervious Cover in a Watershed in South Central Pennsylvania.* **Joseph McNally** (Principal Hydrogeologist, GeoServices, Ltd., Camp Hill, PA).
- (2:35-2:50). *Estimates of Long-Term Mean Annual Groundwater Recharge Rates in Pennsylvania.* **Dennis Risser** (U.S. Geological Survey, New Cumberland, PA) and Stuart Reese (Pennsylvania Geological Survey).

**2:55 – 4:45, Contemporary Water Issues and Potential Solutions.** Session moderator: **Mira Olson** (Professor, Dept. of Civil, Environmental, & Architectural Engineering, Drexel University)

- (2:55-3:10). *Emerging Contaminants in Pennsylvania Waters: What and So What.* **Arianne Proctor**, J. Kent Crawford and Andrew G. Reif (Pennsylvania Water Science Center, US Geological Survey, New Cumberland, PA).
- (3:15-3:30). *Using Living Machines to Remove Endocrine Disruptors From Wastewater.* **Rachel Brennan** (Assistant Professor, Dept. of Environmental Engineering, Penn State University)

**3:35– 3:50, Break.**

- (3:50-4:05). *The Case for Cumulative Impact Assessment for the Extraction of Natural Gas from Marcellus Shale.* **Michel Boufadel**, (Professor & Chair, Dept. of Civil & Environmental Engineering, Temple University, Philadelphia, PA).
- (4:10-4:25). *Membrane Treatment of Marcellus Shale Flowback Wastewater.* **Kevin Gilmore** (Assistant Professor, Dept. of Civil & Environmental Engineering, Bucknell University).
- (4:30-4:45). *Interaction Between Groundwater and Surface Water Resources in Pennsylvania Headwaters Occupied by Marcellus Shale Gas Wells.* **Jim Richenderfer** (Senior Scientist, Susquehanna River Basin Commission).

**4:50– 5:00, Wrap-Up.**

- (4:50-5:00). *Closing Remarks.* **Jeffrey Featherstone** (Professor, Dept. of Community and Regional Planning, Temple School of Environmental Design, Ambler, PA).

# **USGS Summer Intern Program**

None.

<b>Student Support</b>					
<b>Category</b>	<b>Section 104 Base Grant</b>	<b>Section 104 NCGP Award</b>	<b>NIWR-USGS Internship</b>	<b>Supplemental Awards</b>	<b>Total</b>
<b>Undergraduate</b>	0	0	0	0	0
<b>Masters</b>	5	0	0	1	6
<b>Ph.D.</b>	2	0	0	0	2
<b>Post-Doc.</b>	1	0	0	0	1
<b>Total</b>	8	0	0	1	9

## **Notable Awards and Achievements**

Regarding the project entitled Public Education on Water Issues Related to Marcellus Gas Drilling, led by Bryan Swistock at Penn State University: the principal investigators received the Penn State Extension, Team Award at the Extension Annual Conference in Altoona, PA in November, 2010 for their work on the Extension Safe Drinking Water Team. Much of this award was related to programs developed as a result of this project, aimed at helping private water system owners in the Marcellus region of the state.

Regarding the project entitled Coupled Analytical and Biological Analysis of Endocrine Disrupting Compounds (EDCs) of Emerging Concern in Municipal Wastewater Sources in Philadelphia, led by Mohan Achary at Temple University: doctoral student Candace Johnson won first place for her presentation at the Society and Environmental Toxicology Hudson Delaware Regional Chapter, 26th Annual Meeting.